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EFFECT OF MOLECULAR STRUCTURE ON THE ELECTROOPTIC PERFORMANCE OF ELECTROCLINIC LIQUID CRYSTALS

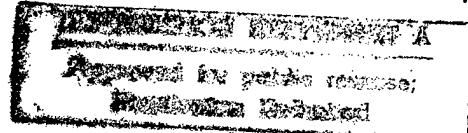
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Abstract The correlation between molecular structure and electrooptic performance is studied for novel room temperature chiral smectic A liquid crystals. It is observed that slight modifications of the hydrocarbon chain connected to the chiral center result in dramatic differences in their electrooptic performance. If the hydrocarbon chain is shortened or if a double bond is localized at the end of the hydrocarbon chain, the tilt angle, electroclinic coefficient, and switching time are significantly suppressed.

INTRODUCTION

In 1977, Garoff and Meyer observed the electroclinic effect above the smectic-A-smectic C* phase in liquid crystalline materials composed of chiral molecules.^{1,2} In this effect, the electric field applied parallel to the plane of the smectic layers couples to the transverse molecular dipole moment. Since the molecules lack inversion symmetry, a molecular tilt is realized in a plane perpendicular to the electric field. The electroclinic effect has been studied in the bulk chiral smectic A,³⁻⁵ higher-order orthogonal smectic phases,⁶ nematic phases,⁷ and has even been established to exist at a solid interface.^{8,9} Apart from their interesting basic properties, electroclinic materials are promising for applications, such as spatial light modulators,¹⁰ that require analog phase modulation capability (gray scale) and fast switching times. Evolution of this technology will greatly depend on the synthesis of electroclinic materials with large induced tilt angles and electroclinic coefficients, field-independent and fast switching times, and a broad temperature range stable down to sub-ambient temperatures.

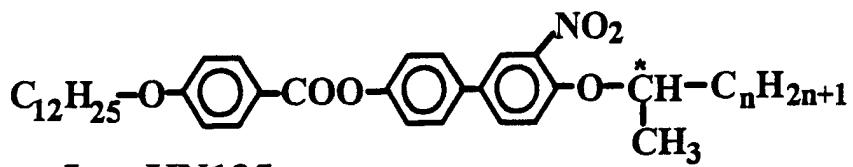


Development of materials with large electroclinic tilt angles needed for applications requires a fundamental understanding of the relationship between the molecular structure and the magnitude of the induced tilt angle.¹¹⁻¹³ Bahr, Heppke, and Klemke¹¹ studied a homologous of materials to probe the relationship between molecular structure and the electrooptic performance. They observed that a longer alkyl chain on the non-chiral end resulted in a larger electroclinic tilt angle. More recently, we have also observed a similar phenomena in three successive even members of the KN homologous series.^{12,13} These materials are unusual because of their large induced tilt angles in a broad temperature range with no underlying smectic C* phase⁴ which is known to enhance field-induced tilt angles.¹⁴ Walba and coworkers¹⁵ have prepared mixtures of electroclinic materials to enhance the tilt angle.

In this contribution we present results of our electrooptic studies. The results show a slight decrease in the chain length connected to the chiral center leads to a significant reduction in the molecular tilt angle and electroclinic coefficient. A similar behavior is found to occur if a double bond is localized at the end of the hydrocarbon chain connected to the chiral center.

EXPERIMENTAL

Four members of the homologous series which we refer to as KN compounds were studied. The structural formula and phase transition temperatures are presented in Figure 1 and Table I. The desirable feature of these materials is that they all exhibit chiral smectic A phases (identified by optical microscopy) to sub-ambient temperatures. No crystallization was observed in any of the samples when they were maintained at room temperatures. Their broad chiral smectic A temperature range is likely due to the proximity of the chiral center to the aromatic core and the presence of the laterally substituted nitro group which prohibits chiral smectic C* formation. Also in these materials the chiral methyl group is very close to the lateral nitro substitute so that the relative rotations of these two moieties about the long axis of the molecule are highly hindered. This steric hindrance most likely results in large dipolar coupling and therefore a large induced tilt angle as we shall see later.



$n=5$ KN125

$n=3$ KN123

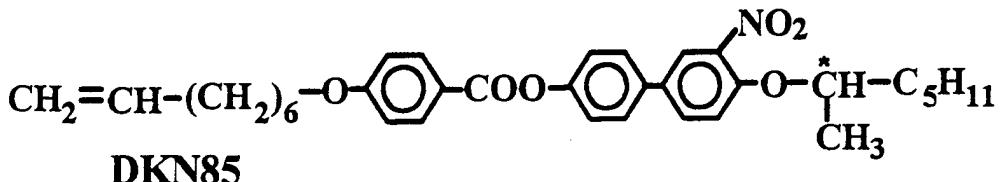
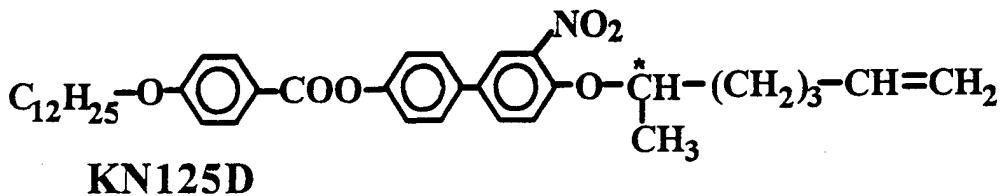


FIGURE 1 Molecular structure of electroclinic materials

TABLE 1 Phase transition temperatures for the KN materials upon heating. The crystal and isotropic phases are denoted by K and I, respectively. The presence of a double bond is represented by a D in the sample identification.

Sample	Transition Temperatures (°C)
KN125	K 29.8 chiral Sm A 80.0 I
KN123	K <5 chiral Sm A 81.4 I
KN125D	K 33.2 chiral Sm A 73.5 I
DKN85	K 27.5 chiral Sm A 61.1 I

For electrooptic studies and tilt angle measurements, the materials were loaded into prefabricated 10 μm commercially available samples cells (E.H.C., Japan) without further processing. The indium tin oxide (ITO) coated glass plates had an overlying

rubbed polyimide alignment layer to facilitate uniform planar alignment. The temperature of the sample was controlled in a Mettler hot stage.

The electric field induced molecular tilt angle, θ , was measured by monitoring the concomitant change in relative intensity, ΔI , and zero-field intensity, I_0 , when the homogeneously aligned sample was oriented between crossed polarizers with the first polarizer being oriented at an angle γ with respect to the director in the absence of the field as depicted in Figure 2. By orienting the sample at an angle $\gamma=\pi/8$, the tilt angle can be readily derived by the simplified expression $\theta=\sin^{-1}(\Delta I/I_0)/4$, where $\Delta I=I_{\max}-I_{\min}$ corresponds to the difference between the maximum, $I_{\max}(V_0)$, and minimum, $I_{\min}(-V_0)$, intensity at a voltage V_0 and $-V_0$.¹⁶ The $\gamma=\pi/8$ orientation of the sample was chosen because it is most sensitive to the angular position of the director, therefore enabling even small tilt angles to be determined precisely. The transmitted light intensity through the sample was monitored with a photodiode and digital oscilloscope. We have recently modified the analysis of the measured intensity to derive the molecular tilt angle even if the quasi-bookshelf stripe texture is present.¹⁷ This correction becomes important for materials with a large induced tilt angle (large electric fields) and is negligible for small tilt angles. However, this requires additional information on the quasi-bookshelf geometry which is only accessible with x-ray diffraction techniques; therefore, we assume the bookshelf structure to derive our tilt angles. The tilt angle measurements were also checked by manually rotating the sample between crossed polarizers and identifying the extinction states corresponding to $+V_0$ and $-V_0$ to ensure the accuracy of our intensity measurements.

RESULTS AND DISCUSSION

The initial studies on electroclinic materials^{4,11-13,15} prompted us to investigate the effects on the electrooptic performance of KN materials if the hydrocarbon chain on the chiral end is modified. The molecular tilt angle as a function of electric field is presented in Figure 3. There are two direct comparisons which can be made: the KN125 and KN125D, and the KN125 and KN123. Both modifications on the chiral

side of the molecule result in dramatic effects on the magnitude of the molecular tilt angle. It also affects the electroclinic coefficient, $d\theta/dE$.

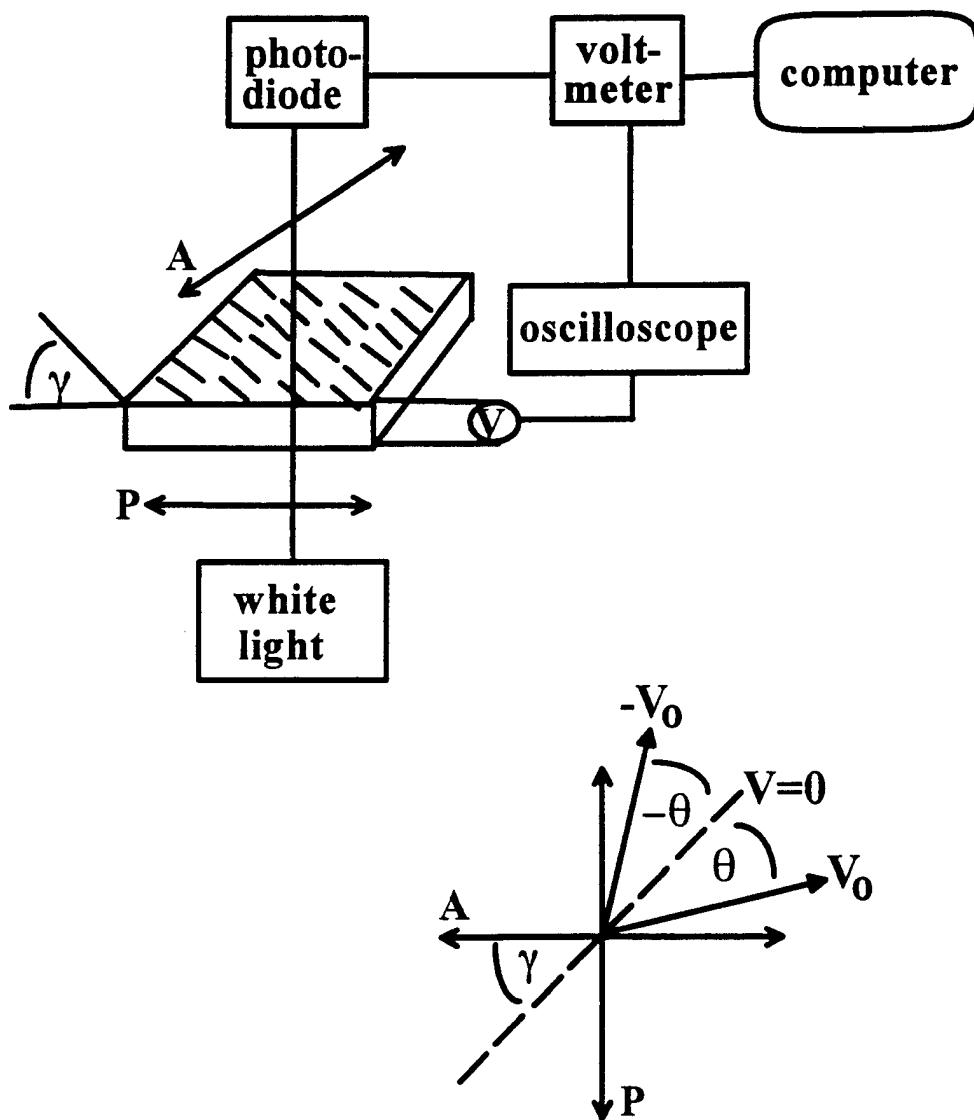


FIGURE 2 Experimental apparatus for electrooptic characterization.

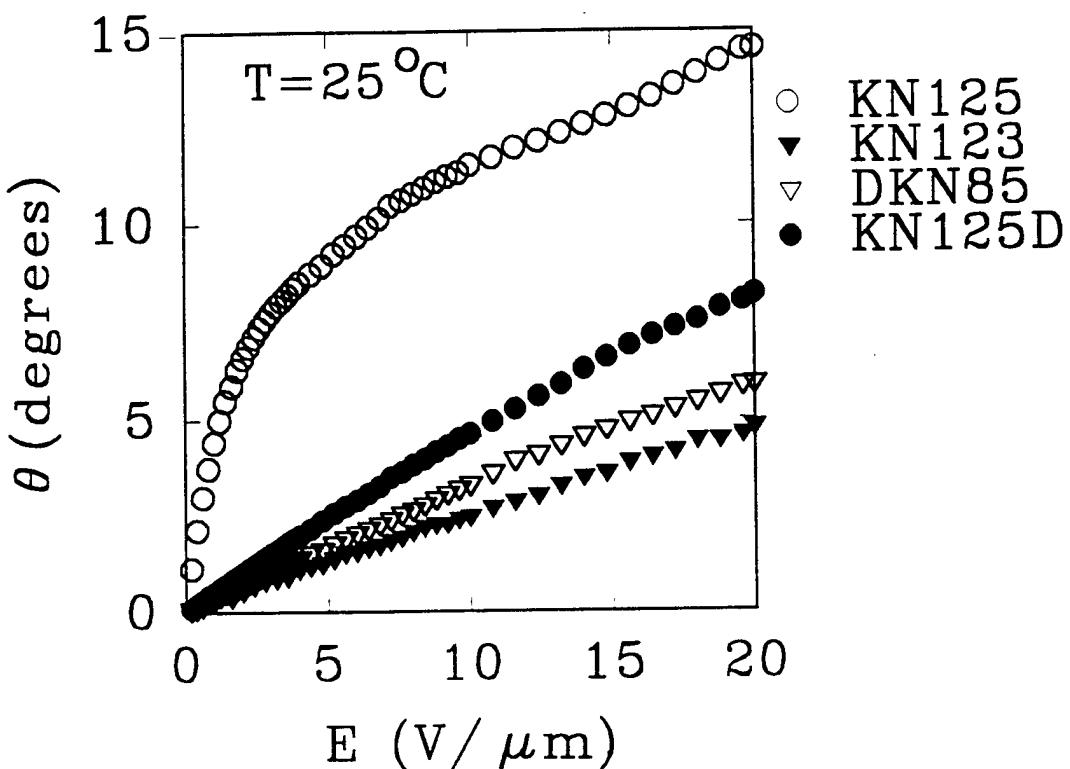


Figure 3 Molecular tilt angle as a function of electric field at $T=25^{\circ}\text{C}$.

Before proceeding with the comparison of the electrooptic performance of the electroclinic materials in Table I, it is worthwhile to review the predictions of phenomenological theories. It has been shown that the tilt angle varies linearly and obeys the following expression $\theta=cE/\alpha(T-T_c)$ for small tilt angles where c is often called the electroclinic coefficient, α is a phenomenological constant associated with the leading term in the free energy expansion, and T_c is the temperature where the smectic C* phase appears. Lee and Patel¹⁶ showed that higher order θ terms in the free energy resulted in a $\theta \sim E^{1/3}$ dependence and demonstrated this behavior with a commercial electroclinic mixture.¹⁶ The slope of the θ versus E curve is proportional to the electroclinic coefficient and is given by $d\theta/dE=c/\alpha(T-T_c)$. The switching time, τ , in electroclinic materials is predicted to be field independent, $\tau=\eta/\alpha(T-T_c)$, in the first approximation, where η is the tilt viscosity. Abdulhalim and Moddel¹⁸ have included higher order terms in θ and showed that τ has a slight field dependence for large values of θ .

The first comparison to make in Figure 3 is between KN125 and KN123. Decreasing the hydrocarbon chain on the chiral side by two $-\text{CH}_2-$ units results in a substantial decrease in the molecular tilt angle and changes the profile of the θ versus E curves. The tilt angle for the KN125 material starts out very linear and increases less rapidly at $E=3 \text{ V}/\mu\text{m}$ eventually reaching a value of $\theta \sim 15^\circ$ at $E=20 \text{ V}/\mu\text{m}$; however, the KN123 tilt angle maintains a very linear profile for fields up to $E=20 \text{ V}/\mu\text{m}$ but only reaches a tilt angle of $\theta \sim 5^\circ$. The value of $d\theta/dE$ is also substantially reduced for KN123, $d\theta/dE=0.27 \text{ }^\circ/(\text{V}/\mu\text{m})$, compared to $d\theta/dE=4.7 \text{ }^\circ/(\text{V}/\mu\text{m})$ for KN125 at low fields. A similar comparison can be made between KN125 and KN125D. When a double bond is localized at the end of the hydrocarbon chain connected to the chiral center (KN125D), a significant reduction in the tilt angle occurs. In addition, the profile of the θ versus E curve for KN125D is linear for electric fields as large as $E=20 \text{ V}/\mu\text{m}$ with a tilt angle of $\theta=8^\circ$. The electroclinic coefficient is also much smaller for the KN125D, $d\theta/dE=0.50 \text{ }^\circ/(\text{V}/\mu\text{m})$, as compared to that for KN125. We have also included DKN85, which does not have a direct comparison with the other materials, in Figure 3. It also has a very linear profile with a tilt angle $\theta=6^\circ$ at $E=20 \text{ V}/\mu\text{m}$ with a electroclinic coefficient of $d\theta/dE=0.34 \text{ }^\circ/(\text{V}/\mu\text{m})$. The low θ value is consistent with the effect of the decrease in the chain length on the nonchiral end compared to KN125. However, the effect of the double bond on the decrease cannot be commented upon without a comparison to the same compound without a double bond.

The switching time, τ , was measured by recording the optical response of the material as it traversed from $-\theta$ to $+\theta$ (using a bipolar pulse from $-V_o$ to $+V_o$), as the time that elapsed from the 90% transmission state to the 10% transmission state. The switching dynamics are presented in Figure 4. It is very apparent from Figure 4 that the switching dynamics are significantly different for the KN125 compounds, as compared to the other three materials KN125D, KN123, and DKN85. The value of τ for the KN125 compound is found to be strongly dependent on the electric field, whereas the other compounds exhibit field independent switching behaviors. The field

independent switching behaviors (as well as the linear electroclinic effect as shown in Figure 3) are consistent with pure electroclinic switching. The strong field dependence of the KN125 compounds opens up some very interesting questions on the nature of the dynamics in this material and being currently addressed by electrooptic and dynamic light scattering techniques.¹⁹

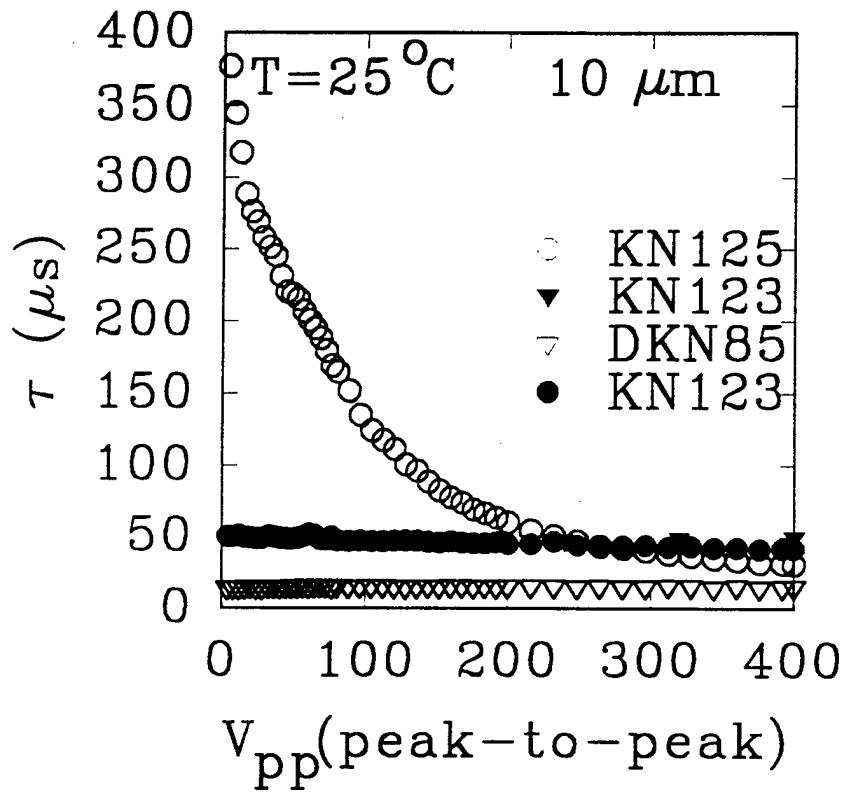


Figure 4 The switching time as a function of applied voltage at $T=25^{\circ}\text{C}$ where V_{pp} corresponds to the peak-to-peak voltage.

CONCLUSIONS

We have studied the electroclinic effect in materials where the hydrocarbon chain connected to the chiral center is varied. We find that the electrooptic performance strongly depends on the length and nature of this hydrocarbon chain. The molecular tilt angle and the electroclinic coefficient were found to decrease with decreasing chain length. Also when a double bond is localized at the end of the hydrocarbon chain

connected to the chiral center, the tilt angle and electroclinic coefficient were found to also decrease. This is the first study of this kind which provides information on the correlation between the molecular structure and the electrooptic parameters when the molecule is manipulated on the chiral side. All materials presented here were stable at ambient temperatures, and therefore, have great potential for applications.

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